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Standard Method of Test for
DILUTE-SOLUTION VISCOSITY OF POLYMERS[1]

This Standard is issued under the fixed designation D 2857; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This method covers the determination of the dilute-solution viscosity of polymers. It is applicable to all polymers that dissolve completely without chemical reaction or degradation to form solutions that are stable with time at a temperature between ambient and approximately 150 C. Results of the test are usually expressed as viscosity ratio, logarithmic viscosity number, or limiting viscosity number and directions for determining these quantities are given.

NOTE 1—The following two sets of nomenclature are commonly used to describe the dilute-solution viscosity of polymers:

Recommended Term[2]	Former Term[3]
viscosity ratio	relative viscosity
viscosity number	reduced viscosity
logarithmic viscosity number	inherent viscosity
limiting viscosity number	intrinsic viscosity

In this method, only the recommended terms are used.

2. Significance

2.1 The determination of dilute-solution viscosity provides one item of information towards the molecular characterization of polymers. When viscosity data are used in conjunction with other molecular parameters, the properties of polymers depending on their molecular structure may be better predicted.

2.2 With certain restrictions, satisfactory correlations can be obtained between dilute-solution viscosity and molecular parameters such as molecular weight or chain length. The most limiting restrictions which must be observed are as follows:

2.2.1 It must be known that the polymers used to establish the correlations and those to which they are applied do not consist of or contain branched species. Basically a measure of molecular size and not molecular weight, the dilute-solution viscosity can be correlated appropriately with molecular weight or chain length only if there is a unique relationship between the mass and the size of the dissolved polymer molecules. This is the case for linear, but not for most branched, polymers. Caution should be exercised in applying empirical viscosity-molecular weight relationships to polymers of unknown or uncertain structure since unsuspected branching may exist.

2.2.2 For reasons similar to those outlined in 2.2.1, it must be required that the polymers to which the correlations are applied have the same chemical composition as those used in establishing the relationships.

2.3 For polymers meeting the restrictions of 2.2, empirical relationships can be developed between the dilute-solution viscosity of a polymer and its hydrodynamic volume or average chain dimension (radius of gyration or end-to-end distance). Such relationships depend upon any variables influencing this molecular size of the dissolved polymer. The most important of these variables are solvent type and temperature. Thus, the solution viscosity of a given polymer specimen depends on the choice of these variables, and they must always be specified with the viscosity for complete identification.

2.4 The further empirical interpretation of viscosity data in terms of molecular weight rather than size requires control of the variables described in 2.2.

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[1] This specification is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D-20.70 on Analytical Methods.

Effective April 17, 1970.

[2] International Union of Pure and Applied Chemistry, *Journal of Polymer Science*, JPSCA, Vol 8, 1952, p. 257.

[3] Cragg, L. H., *Journal of Colloid Science*, JCSCA, Vol 1, 1946, p. 261.

2.5 The solution viscosity of a polymer of sufficiently high molecular weight may depend on rate of shear in the viscometer, and the viscosity of a polyelectrolyte (polymer containing ionizable chemical groupings) will depend on the composition and ionic strength of the solvent. Special precautions beyond the scope of this method are required when measuring such polymers.

2.6 Finally, the viscosity of polymer solutions may be affected drastically by the presence of recognized or unrecognized additives in the sample, including but not limited to colorants, fillers, or low-molecular-weight species.

3. Apparatus

3.1 *Volumetric Flasks*[4], 100-ml or other size found convenient.

3.2 *Transfer Pipets*[4], sizes between 1 and 25 ml, as required. Transfer pipets for use with polymer solutions should have about 2 mm cut from their lower tips to permit more rapid transfer of the solution to the viscometer.

3.3 *Constant-Temperature Bath*, capable of maintaining ± 0.01 C at the desired operating temperature (usually between 25 and 135 C). Less stringent temperature control (±0.02 C) is satisfactory upon demonstration that the precision of the results is not affected.

3.4 *Viscometer*, glass capillary type, as described in ASTM Specification D 2515, for Kinematic Glass Viscometers,[5] subject to the limitations of Appendixes A-C of that method. Efflux time for the solvent and temperature used shall be greater than 200 s (except that efflux time for semi-micro viscometers shall be greater than 80 s), to eliminate the need for kinetic-energy corrections.

NOTE 2—Two types of viscometers are commonly used: one is a constant-volume device of simple construction, recommended for use where solution viscosity is to be measured at a single concentration, as for determination of the viscosity number or logarithmic viscosity number. It may also serve for the determination of the limiting viscosity number through measurement of several solutions having different concentrations.

The second type viscometer, commonly called a dilution viscometer, is a time-saving device for the determination of limiting viscosity number since it does not require constant liquid volume for operation. Several concentrations of a polymer solution can be tested by adding a known quantity of the solvent at the test temperature directly to the viscometer, mixing, measuring the viscosity, and then making the next dilution. The viscosity of the pure solvent must be measured separately.

An alternative procedure is to start with the minimum volume of the pure solvent, then add aliquots of a concentrated stock solution to the viscometer to obtain values of the viscosity ratio at successively higher concentrations. The choice of procedures is dictated by the range of volumes with which the viscometer will operate and the range of concentrations desired for test.

3.5 *Timer*, graduated in divisions of 0.1 s or less, as described in Section 4(*e*) of ASTM Method D 445, Test for Viscosity of Transparent and Opaque Liquids (Kinematic and Dynamic Viscosities).[5]

3.6 *Thermometer*, suitable for the specified test temperature and conforming to the specifications of ASTM Specification E-1, for ASTM Thermometers,[6] Kinematic Viscosity Thermometers ASTM 110F (for use at 135 C) and 118F (for use at 30 C).

3.7 *Fritted Glass Filter Funnel*, coarse grade[7], or equivalent.

4. Materials

4.1 *Solvents* as required or as recommended in the Appendix.

4.2 *Heat-Transfer Liquid* for constant-temperature bath.

NOTE 3—The following materials have been used as heat transfer liquids: (*1*) silicone oil[8], (*2*) mineral oil, (*3*) peanut oil, (*4*) water, (*5*) water-miscible liquid such as glycerol or ethylene glycol. The material selected must not discolor or smoke on prolonged exposure at the test temperature; in some cases discoloring may be inhibited by the use of an antioxidant. The use of water or a water-miscible liquid facilitates cleaning glassware used in the test.

4.3 *Nitrogen*, for purging.

5. Preparation of Sample

5.1 The sample need not be predried or conditioned unless previous specific knowledge, for example that the material is known to be hydroscopic, makes such pretreatment desirable. (See Appendix.)

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[4] Glassware should conform to the standards of accuracy in National Bureau of Standards Circular No. C602, "Testing of Glass Volumetric Apparatus."

[5] *Annual Book of ASTM Standards*, Part 17.

[6] *Annual Book of ASTM Standards*, Part 30.

[7] A suitable filter type is Corning Glass No. 36060.

[8] Dow Corning Corp., Midland, Mich.; Union Carbide Corp., Linde Silicones Div., New York, N. Y.; General Electric Co., Silicone Products Dept., Waterford, N. Y.

5.2 If it is known that the sample dissolves only slowly in the selected solvent, pretreatment to reduce the particle size of the sample may be advisable.

NOTE 4—Some samples can be pulverized conveniently in a rotary cutting mill with a 20-mesh screen at the outlet of its pulverizing chamber. The Wiley mill, widely available from scientific supply houses, has been found satisfactory. Care must be taken to avoid overheating the sample during pulverization, which might lead to thermal degradation. Low-melting polymers, or hard, tough samples, often can be satisfactorily pulverized only at very low temperature, for example in the presence of dry ice or liquid nitrogen. (See Appendix.)

6. Procedure

6.1 Weigh the sample (see the Appendix for size and tolerance) in a tared 100-ml volumetric flask (or weigh and transfer quantitatively to the flask). If the sample is known to oxidize easily in the subsequent dissolving step, the flask may be purged with nitrogen.

NOTE 5—Other sizes of volumetric flasks may be used, depending on viscometer size and amount of sample available. If another size flask is used, adjust the sample weights and solvent and solution volumes accordingly.

NOTE 6—For greatest reliability of results and in the absence of specific information (see Appendix), select the sample size on the basis of experience to give a viscosity ratio near 1.5. If several concentrations of a solution of a single sample are to be used (Note 7), select them so that the viscosity ratio falls in the range from 1.2 to 2.0.

NOTE 7—Preparation of a single solution may often suffice, either for determining the viscosity ratio or logarithmic viscosity number, or as a stock solution for use in a dilution viscometer to determine the limiting viscosity number. If more than one solution concentration is desired, weigh a series of specimens (often four) into separate flasks, selecting the specimen weights to give the desired solution concentration. Duplicate specimens may be prepared if desired.

6.2 Add approximately 50 ml of solvent to each specimen flask, purge with nitrogen if necessary, and shake the flask once every 10 min until solution is complete (alternatively, use a laboratory shaker). Elevated temperature may enhance solution rate (see Appendix) but should be used with caution since some polymers and solvents have limited high-temperature stability. If solution is carried out at an elevated temperature, subject a flask of pure solvent to the same conditions as the polymer solution.

NOTE 8: **Caution**—Complete solution of all of the specimen is essential. When solution appears complete, examine the flask with care to be sure that no undissolved material, gel particles, or foreign matter is present.

6.3 Place the volumetric flasks containing the solution(s) and the pure solvent in the constant-temperature bath maintained at the test temperature. Add solvent to the solution flask(s) to a total volume of about 99 ml, using solvent maintained at the bath temperature. Mix the solution(s) thoroughly, and replace in the bath. After temperature equilibrium has been achieved (10 to 30 min) complete the dilution to the 100-ml mark by adding solvent maintained at the test temperature, using a transfer pipet. Mix the contents of the flask(s) thoroughly.

NOTE 9: **Caution**—Be sure that the solution is uniformly mixed. If the test temperature is above ambient, avoid cooling the flask excessively while mixing.

6.4 Where necessary to prevent oxidation, purge the viscometer with a slow stream of nitrogen. With the viscometer permanently positioned in the constant-temperature bath at the required temperature, transfer a suitable amount of solution into the viscometer using a suitably modified transfer pipet (3.2). The amount varies with the type of viscometer used (Note 2). If necessary, filter the solution through a fritted-glass filter or equivalent into the viscometer taking care not to lose solvent in the process (pressure filtration). Filtration is usually desirable.

NOTE 10—If the solution is to be handled at elevated temperatures, the transfer pipet may be fitted with a suitable heating mantle to retard precipitation of polymer from the solution during the transfer.

6.5 After temperature equilibration has been achieved (a minimum of 10 min), bring the liquid level in the viscometer above the upper graduation mark by means of gentle air (or, preferably, nitrogen) pressure applied to the arm opposite the capillary. Allow the solution to drain down through the capillary. Start the timer exactly as the meniscus passes the upper graduation mark, and stop it exactly as the meniscus passes the lower mark.

6.6 Determine the efflux time (step 6.5) at least three times each for the solution and for the pure solvent. Three consecutive readings should agree to within 0.1 s or 0.1 percent of their mean, whichever is greater. Larger variations may result from foreign material in the viscometer or from inadequate temperature control, and require repetition of the experiment after their cause is located and corrected.

7. Calculations

7.1 *Viscosity Ratio*—calculate the viscosity ratio from the average efflux time for the solvent, t_0, and the average efflux time for the solution, t, as follows:

$$\text{Viscosity Ratio} = t/t_0$$

NOTE 11—Strictly, the viscosity ratio is defined as η/η_0 where η and η_0 are the viscosities of the solution and solvent, respectively, and are related to the corresponding efflux times by:

$$\eta = Ct\rho - E\rho/t^2$$
$$\eta_0 = Ct_0\rho_0 - E\rho_0/t_0^2$$

where C and E are constants for the particular viscometer used. The equation in 7.1 follows if the second term in these relations, a kinetic-energy correction, is negligible and the respective solvent and solution densities, ρ_0 and ρ, are substantially equal. This kinetic energy correction is negligible for the recommended viscometers and efflux times (see 3.4)[9].

7.2 *Logarithmic Viscosity Number*—calculate the logarithmic viscosity ratio for each solution concentration as follows:

$$\text{Logarithmic Viscosity Number} = \ln(\eta/\eta_0)/c$$

where $\ln(\eta/\eta_0)$ is the natural logarithm of the viscosity ratio and c is the solution concentration in grams per milliliter (grams per milliliter of solution). The units of logarithmic viscosity number are, therefore, ml/g.

7.3 *Limiting Viscosity Number*—Plot the logarithmic viscosity number versus concentration, for several solution concentrations, on rectilinear graph paper. Draw the best straight line through the points and extrapolate it to zero concentration. The limiting viscosity number, $[\eta]$, is the intercept of the line at zero concentration. The units of the limiting viscosity number are ml/g.

NOTE 12—The viscosity number, $(\eta - \eta_0)/\eta_0 c$ may be calculated and plotted versus concentration on the same graph with the logarithmic viscosity number. The two lines should extrapolate to the same point (the limiting viscosity number) at $c = 0$; plotting both functions may serve to fix the limiting viscosity number with greater accuracy. If the limitation on viscosity ratio stated in Note 6 is observed, the extrapolation lines should be accurately straight.

NOTE 13—For some polymer-solvent systems, it can be demonstrated that the slopes of the lines of viscosity number and logarithmic viscosity number versus concentration are closely similar for all samples normally encountered. For such systems, two of which are described in the Appendix, the limiting viscosity number can be approximated from data obtained at a single concentration by one of the formulas tabulated by Billmeyer[10].

8. Precision and Accuracy

8.1 For most polymer-solvent systems, the logarithmic and limiting viscosity numbers can be determined with a standard deviation for reproducibility of about 1.0 ml/g. Since the viscosity numbers are available only from these measurements, accuracy of their values has no meaning.

9. Report

9.1 The report shall include the following:

9.1.1 Complete identification of the sample tested.

9.1.2 Conditioning procedure, if any.

9.1.3 One or more of the following:

9.1.3.1 The viscosity ratio, given to one significant figure beyond the decimal point, followed by the concentration of the test solution in g/ml.

9.1.3.2 The logarithmic viscosity number in ml/g, carried to one significant figure beyond the decimal point, followed by the concentration of the test solution in g/ml.

9.1.3.3 The limiting viscosity number in ml/g, carried to the decimal point.

9.1.4 The solvent employed and the test temperature.

NOTE 14—ISO Draft Recommendation No. 1628, Directives For The Standardization of Methods For The Determination of The Dilute Solution Viscosity of Polymers, differs from this method in several respects. These are:

(1) Application of kinetic energy corrections are different such that errors in viscosity ratios may be as high as 3 percent depending on flow times and viscometer type.

(2) The recommended test temperature is 25 ± 0.05 C.

It is therefore recommended that caution be exercised when comparing data obtained by both methods.

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[9] Cannon, M. R., Manning, R. E., and Bell, J. D., *Analytical Chemistry*, ANCHA, Vol 32, 1960, p. 355.

[10] Billmeyer, F. W., Jr., *Journal of Polymer Science*, JPSCA, Vol 4, 1949, p. 83.

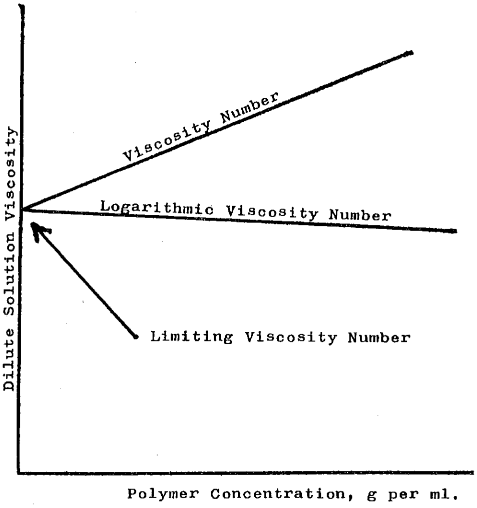

FIG. 1 Example of Plot to Determine Limiting Viscosity Number.

APPENDIX

A1. DETAILS OF MATERIALS AND PROCEDURES FOR IMPORTANT POLYMER TYPES

A1.1 Polyamide

A1.1.1 Recommended solvents are formic acid (90 ± 0.2 percent in water) or *m*-cresol, melting point 11 to 12 C.

A1.1.2 Recommended dissolving conditions are: for formic acid, 30 C; for *m*-cresol, 2 h max at 95 to 100 C or 8 h at 50 C.

A1.1.3 The recommended test temperature is 30 C.

A1.1.4 The recommended solution concentration is 0.0050 ± 0.00002 g/ml.

A1.2 Polycarbonate

A1.2.1 Recommended solvents are methylene chloride or purified grade and dry *p*-dioxane.

A1.2.2 Recommended dissolving temperatures are: for methylene chloride, 30 C; for *p*-dioxane, 60 C.

A1.2.3 If pigments or other fillers are present, the resin may be dissolved in methylene chloride and the solution filtered. The methylene chloride may be evaporated from the resulting clear solution to leave the resin in the form of a thin film. After this has been dried for several hours at 125 C, samples may be taken for viscosity measurement.

A1.2.4 The recommended test temperature is 30 C.

A1.2.5 The recommended solution concentration is 0.0040 ± 0.0002 g/ml, or by convenient dilution from 0.010 ± 0.00002 g/ml.

A1.3 Polyethylene

A1.3.1 *Scope*—Measurement of the dilute-solution viscosity of ethylene polymers presents problems not ordinarily encountered in viscometry, since these polymers are not soluble in any known liquid at room temperature, and some of the higher-density materials are insoluble below 100 C. Accordingly, extreme care must be taken in all operations, such as transferring solution to the viscometer, to avoid loss of polymer from the solution by precipitation. In addition, some ethylene polymers have significant amounts of gel; this test has little significance unless the sample is completely soluble. With these limitations, the method is applicable to ethylene polymers of any density, the usual range being from 0.91 to 0.97 g/cm^3.

A1.3.2 *Apparatus*—In addition to the apparatus described in Section 3, it is convenient to have available an oven maintained at 140 ± 5 C.

NOTE A1—A viscometer especially designed for high temperature operation[11] may be found useful.

A1.3.3 *Solvent*—The recommended solvent is decahydronaphthalene, practical grade, purified and redistilled as follows:

A1.3.3.1 Purify the solvent by percolation through 100 to 200-mesh silica gel, commercial grade, to remove naphthalenes, tetrahydronaphthalene, peroxides, and other oxy compounds.

A1.3.3.2 Distill in accordance with ASTM Method D 86, Test for Distillation of Petroleum Products:[5]

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[11] Schulken, R. M., and Sparks, M. L., *Journal of Polymer Science*, JPSCA, Vol 26, 1957, p. 227.

Initial boiling point (760 mm Hg)	190 C min
10 percent	191 C min
20 percent	192 C min
80 percent	194 C max
90 percent	195 C max
Dry point	196 C max

A1.3.3.3 Immediately after distillation, add 0.05 to 0.1 weight percent of an antioxidant. Phenyl-β-naphthylamine and 4-methyl-2,6-ditertiary-butylphenol have been found satisfactory and render the solvent and solutions of most ethylene polymers resistant to oxidation at 135 C for many hours.

A1.3.3.4 Other recommended solvents are 1,2,3,4-tetrahydronaphthalene and xylene (mixed isomers); but see 2.3.

A1.3.4 *Procedure:*

A1.3.4.1 The recommended dissolving conditions are 140 ± 5 C for 2 to 6 h.

NOTE A2: **Caution**—Dissolution should not be prolonged past 6 h because of the possibility of significant oxidation of the polymer. Extreme care should be taken to ascertain whether solution is complete, see Note 8.

A1.3.4.2 The recommended test temperature is 135 C.

A1.3.4.3 The recommended solution concentration is 0.0020 ± 0.00002 g/ml, or convenient dilution from 0.0040 ± 0.00002 g/ml.

A1.4 Poly(Ethylene Terephthalate)

A1.4.1 Recommended solvents are *o*-chlorophenol (melting point 0 C) or a mixture of 1 part trifluoroacetic acid and 3 parts dichloromethane. Solvents must contain less than 0.15 percent water.

NOTE A3: **Caution**—Since *o*-Chlorophenol is toxic, appropriate measures must be taken to avoid breathing its vapors or contact of the liquid with skin or eyes.

A1.4.2 The samples must be dried to a water content of 0.03 percent or less. Drying may be carried out at 100 C for about 3 h under a pressure of 1 mm Hg or less.

A1.4.3 Recommended dissolving conditions are 2 to 3 h at 90 to 100 C.

A1.4.4 The recommended test temperature is 30 C.

A1.4.5 The recommended solution concentration is 0.0050 ± 0.00002 g/ml.

A1.5 Poly(Methyl Methacrylate)

A1.5.1 Recommended solvent is 1,2-dichloroethane (ethylene dichloride), reagent grade.

A1.5.2 Pretreatment of the sample should not include cutting or grinding in such a way as to cause shear degradation of the polymer.

A1.5.3 Recommended dissolving conditions are 24 h at 30 C.

A1.5.4 The recommended test temperature is 30 C.

A1.5.5 The recommended solution concentration is 0.0020 ± 0.00002 g/ml; but the recommendations of Note 6 should be construed to supersede this.

NOTE A4—The limiting viscosity number may be estimated from data obtained at a single concentration by use of the following equation[10]:

$$[\eta] = (2^{1/2}/c)[(\eta/\eta_0) - 1 - \ln(\eta/\eta_0)]^{1/2}$$

A1.6 Poly(Vinyl Chloride)

A1.6.1 The recommended solvent is cyclohexanone, boiling point 155 to 156 C (760 mm Hg).

A1.6.2 Samples should be dried to a moisture content below 0.1 percent.

A1.6.3 The recommended dissolving temperature is 85 ± 10 C.

A1.6.4 The recommended test temperature is 30 C.

A1.6.5 The recommended solution concentration is 0.0020 ± 0.00002 g/ml.

NOTE A5—The limiting viscosity number may be estimated from data obtained at a single concentration by use of the following equation[10].

$$[\eta] = 1/4\ [(\eta - \eta_0)/\eta_0 c] + 3/4\ [\ln(\eta/\eta_0)/c]$$

A1.6.6 *Precision:*

A1.6.6.1 *Repeatability*—Duplicate results by the same analyst should not be considered suspect unless they differ by more than 1 percent.

A1.6.6.2 *Reproducibility*—The average result of two determinations reported by one laboratory should not be considered suspect unless it differs from that of another laboratory by more than 2 percent.